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# POSITRONIUM FORMATION IN MOLECULAR GASES — FROM EXPERIMENT TO MODELING*

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Results of positron annihilation lifetime measurements of three organic liquids: benzene ($C_6H_6$), cyclohexane ($C_6H_{12}$) and methanol ($CH_3OH$) are reported. The lifetime spectra are acquired at several temperatures for non-degassed, degassed and oxygen-saturated samples. The influence of oxygen on each lifetime and intensity component is discussed. Comparison of lifetime components with experiments in gas phase is done.

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## 1. Introduction

Development of medical imaging techniques based on positron annihilation [1] provides a vastness of new diagnostic methods. The combination of traditional time-of-flight positron emission tomography (TOF-PET) with the positron annihilation lifetime spectroscopy (PALS) [2, 3] opens a broad gate of possibilities to characterize pathological changes occurring in single cells. An accurate interpretation of acquired images requires detailed knowledge about positron behavior in biologically relevant matter.

One of capabilities to be explored with a new generation of TOF-PETs is monitoring of oxygen level in biological tissues. This could be particularly important in the context of cancer diagnosis since it was shown [4] that low levels of tissue oxygenation cause an increased uptake of glucose. Gamma-rays that are acquired during the imaging procedure originate mainly from annihilation of ortho-positronium (o-Ps), *i.e.* a long-lived (142 ns in vacuum) positron bound system in the triplet state. In matter this lifetime is significanly shortened due to annihilation with an electron from surroundings (so-called pick-off annihilation) [5]. Measurements of o-Ps lifetime allow to determine free volumes in which positron is trapped [6, 7].

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Already pioneer PALS studies showed that the presence of $O_2$ decreases significantly the o-Ps lifetime [5, 8]. This effect is observed in both liquid and porous solid bodies [5, 6]. The quenching of o-Ps is usually explained by paramagnetic properties of $O_2$ molecule leading to ortho–para conversion, *i.e.* the spin-flip from triplet to singlet state resulting from exchange of the positronium electron with the single odd unpaired electron of $O_2$ molecule [9]. Consequently, the longest component in PAL spectrum is drastically decreased. This interpretation is supported by the fact that no similar lifetime quenching is caused by diamagnetic molecules such as $N_2$ [10].

Although the influence of oxygen is a well-known fact, little quantitative data exist. There are practically no information on o-Ps lifetimes and intensities as a function of oxygen content at different physical conditions (temperature, presence of magnetic and electric fields). Most of experimental data come from relatively old papers (*e.g.* [8]) using PAL spectrometers with inferior time resolutions when compared with currently available. Consequently, the o-Ps lifetimes were usually derived through a two-component decomposition of PAL spectra. Novel coincidence systems allow to resolve at least three different annihilation routes in organic liquids and solids. There are still no quantitative data about $O_2$ influence on the behavior of other annihilation channels — different from the pick-off process of o-Ps.

An alternative technique for studies of positron–molecule interactions is scattering in gas phase [11]. Total cross sections (TCS) that reflect an overall interaction between the positron and a molecule (ionization, electronic and vibrational excitation, formation of free positronium) can be measured down to almost thermal energies [12, 13]. However, trials to correlate cross sections in gas phase with PALS in liquid phase are sporadic [14].

In the present work, we report the results of positron annihilation lifetime measurements for three organic liquids: benzene ($C_6H_6$), cyclohexane ($C_6H_{12}$) and methanol ($CH_3OH$). Differently from our previous study [15], at present, PAL spectra were acquired at different temperatures for non-degassed, degassed and oxygen-saturated samples. The goal of this work is to initiate more quantitative studies on positron annihilation with respect to the oxygen content in organic materials, and to search possible relations between cross sections in gas phase and positron lifetime components.

## 2. Experimental setup

The positron annihilation lifetime spectra (PALS) were measured using the fast–fast coincidence ORTEC PLS system equipped with plastic scintillators (St. Gobain BC418) and RCA 8850 photomultipliers [16]. The prompt time resolution of the system was 180 ps in full width at half maximum. The positron source $^{22}$Na with activity 10 $\mu$Ci was tightly sealed in 7 $\mu$m thick envelope made of Kapton foil. The source was immersed in studied liquids that were placed inside the vacuum cell. The temperature of the cell was controlled by Peltier cooler. Measurements were carried out as a function of temperature in three regimes: *(i)* in presence of air under atmospheric pressure, *(ii)* after degassing the cell by a standard freeze-thaw technique, *(iii)* after filling the cell with oxygen at atmospheric pressure, *(iv)* checking again for a degassed cell. At least $10^6$ total counts were accumulated in each measurement.

The analysis of lifetime spectra was realized with the LT package created by Kansy [17]. Three exponential components ascribed to p-Ps decay ($\tau_1, I_1$), annihilation of free positrons ($\tau_2, I_2$), and o-Ps decay ($\tau_3, I_3$) convoluted with the instrumental resolution curve were assumed. The source correction due to positron annihilation in Kapton envelope ($I_s = 14\%$ and $\tau_s = 380$ ps) was applied. The fits of three exponential model to PAL spectra were performed assuming a fixed lifetime value for p-Ps decay, $\tau_1 = 125$ ps that corresponds to its intrinsic lifetime in vacuum; we assumed also a fixed, intrinsic ratio 3:1 between o-Ps and p-Ps intensitied. Nevertheless, it was checked that unconstrained fits do not change the quality of analysis ($\chi^2 < 1.01$) and, in consequence, the general conclusions drawn hereafter.

Total cross sections in gas phase, reported here for the three molecules, were performed on Trento apparatus [18] with enhanced angular and energy resolutions [12] by Karwasz *et al.* [14] and, independently, by Zecca and collaborators [19, 20]. Analysis of cross sections was done by Modified Effective-Range Technique [21, 22]. MERT fit allows to extend cross sections down to zero energy, and to evidence possible structures extending above elastic cross sections [23]. MERT permits also to separate long-range interactions (polarizability of the molecule) from short-range effects, *i.e.* at the distance of valence electrons.

## 3. Results

Values of lifetimes and their intensities at room temperature (293 K) for the three liquids (degassed and oxygenated) are compared in Table I. Present $\tau_3$ (about 3.1 ns) and $I_3$ for all three liquids are consistent with the two-term analysis reported in literature for both non-degassed and degassed samples [8, 24]. Moreover, the present data for the second component $\tau_2$ (about 380–400 ps) and $I_2$ are compatible with the results of three- and four-term analysis reported in Refs. [5, 25–27].

Figure 1 shows results of positron lifetimes $\tau_3$ and $\tau_2$ and corresponding relative intensities $I_3$ and $I_2$ as a function of temperature in non-degassed, degassed and oxygen-saturated samples of benzene (results in cyclohexane

TABLE I

The results of analyses of lifetime spectra for benzene ($C_6H_6$), c-hexane ($C_6H_{12}$) and methanol ($CH_3OH$) at room temperature. Present data for degassed and oxygen-saturated samples are compared with recent review [5].

| Molecule | $\tau_1$ [ns] | $I_1$ [%] | $\tau_2$ [ns] | $I_2$ [%] | $\tau_3$ [ns] | $I_3$ [%] | $I_1+I_3$ [%] |
|---|---|---|---|---|---|---|---|
| **Benzene** | | | | | | | |
| Ref. [5] | 0.142 | 20.5 | 0.440 | 36.4 | 3.18 | 43.1 | 63.6 |
| Degassed | 0.125 | 14.7 | 0.390 | 41.1 | **3.07** | **44.2** | 58.9 |
| Oxygenated | 0.125 | 15.8 | 0.426 | 36.6 | **1.46** | **47.6** | 63.4 |
| **c-hexane** | | | | | | | |
| Ref. [5] | 0.214 | 26.1 | 0.469 | 36.3 | 3.25 | 37.6 | 63.7 |
| Degassed | 0.125 | 12.9 | 0.377 | 48.2 | **3.07** | **38.9** | 51.8 |
| Oxygenated | 0.125 | 13.9 | 0.433 | 44.5 | **1.37** | **41.6** | 55.5 |
| **Methanol** | | | | | | | |
| Degassed | 0.125 | 7.2 | 0.401 | 70.3 | **3.11** | **22.5** | 29.7 |
| Oxygenated | 0.125 | 8.7 | 0.402 | 65.1 | **1.58** | **26.2** | 34.9 |

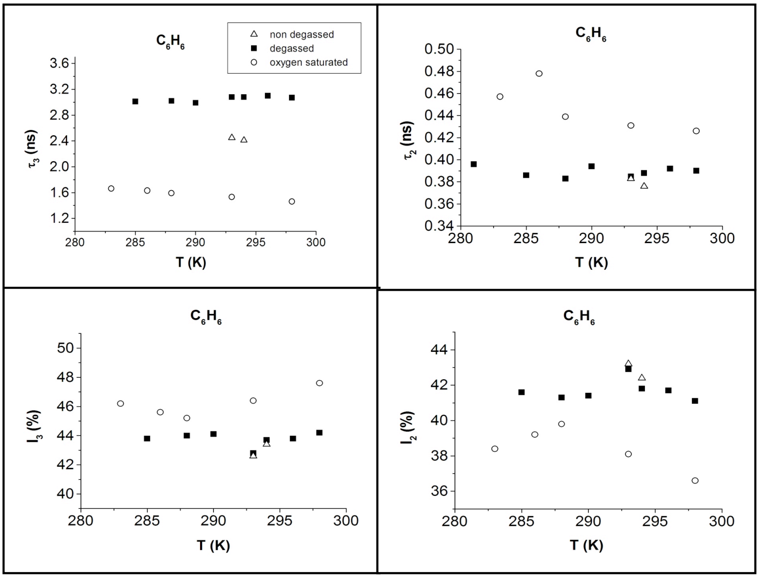

Fig. 1. Positron lifetimes $\tau_3$ and $\tau_2$ and corresponding relative intensities $I_3$ and $I_2$ as a function of temperature in non-degassed (open triangles), degassed (filled squares) and oxygen-saturated (open circles) benzene ($C_6H_6$).

and methanol are similar). All considered parameters depend weakly on the temperature in the considered range (283 K–298 K), where all studied samples are in the liquid phase. However, as expected, presence of oxygen changes significanlty the third (*i.e.* o-Ps) lifetime component (but not much its intensity $I_3$ as we cross-checked releasing the 3:1 o-Ps/p-Ps ratio). For all studied liquids, the $\tau_3$ lifetime falls by almost a factor of two in samples saturated with $O_2$; this difference remains constant *versus* temperature. Furthermore, we checked that in presence of air, $\tau_3$ shows values intermediate between degassed and oxygen saturated samples, and that saturation and degassing processes are fully reversible processes, see Fig. 1. It remains surprising (but in agreement with earlier determinations [5, 7, 8, 24]) that the $\tau_3$ lifetime is the same (within 10% ucertainty of present detemination) for all three molecules, despite of their chemical and physical differences. What makes the difference is the $I_3$ intensity, amounting for $CH_3OH$ only 22%, half of that for $C_6H_6$, see Table I.

In search of possible mechanisms, in Fig. 2 we compare total cross sections for scattering on isolated molecules (*i.e.* in gas phase). Data by two groups (on the same apparatus) demonstrate that cyclohexane and benzene

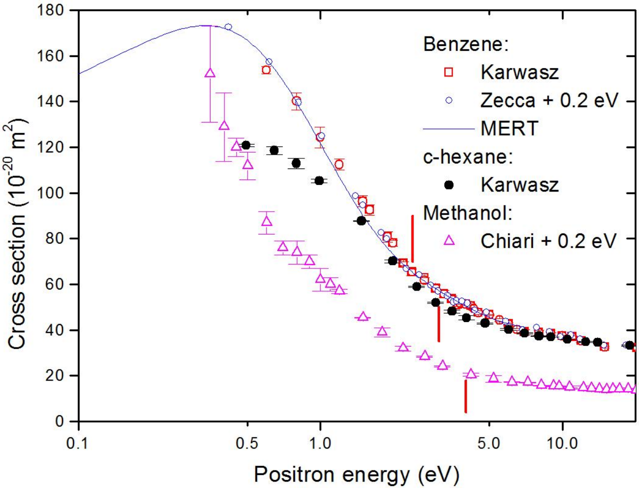

Fig. 2. Total cross sections for positron scattering on benzene, cyclohexane and methanol in gas phase. Data obtained on Trento apparatus [18] by Karwasz *et al.* [14] in benzene (squares with error bars) and cyclohexane (full circles with error bars) and by Zecca and collaborators — benzene [19] (open diamonds) and methanol [20] (triangles with error bars). Zecca's data have been shifted by +0.2 eV, as they used a different energy scaling, see [12]. Line — MERT analysis for benzen from Ref. [21]. Vertical lines show thresholds for positronium formation in gas phase: 2.4 eV, 3.1 eV and 4.0 eV for $C_6H_6$, $C_6H_{12}$ and $CH_3OH$, respectively.

show almost exactly the same values of TCS above relative thresholds for positronium formation, see Fig. 2. In the low energy limit (below 1 eV), benzene cross sections is the highest, but extending it to thermal energies is ambivalent, see [21]. Methanol TCS is the lowest out of the three molecules, but rises sharply in the zero energy limit (methanol posses a perment dipole moment).

How these cross sections relate to lifetimes still remains vague. Karwasz [11] noted that TCS amplitude at the "flat" part (*i.e.* above few eV) would correspond to geometrical dimensions of molecules. This concept was further exploited by Franz, Fedus and Karwasz [29]; then Fedus [30] and independently, Franz [31] showed that flat TCS is caused by trapping positrons in some effective positron–molecule interaction potential, with a quantum well at about the "geometrical dimensions" distance. Zammit *et al.* [32] and Gribakin [33] in *ab initio* calculations for molecular hydrogen and noble gases, respectively, reproduced such flat parts of TCS by introducing inelastic channels, including formation of virtual positronium. Whether a formation of virtual positronium leads to a (real) annihilation signal of o-Ps and p-Ps — we can only speculate.

## 4. Conclusions

The positron annihilation lifetime measurements of three organic liquids: benzene, cyclohexane and methanol were carried out using the fast–fast coincidence system with 180 ps resolution and with analysis into three lifetime components. Differently from polymers [28], positron lifetimes in studied organic liquids practically do not change with temperature. Strong quenching of ortho-positronium (o-Ps) lifetime in presence of oxygen in all studied samples was observed. On the other hand, the o-Ps intensity and the intermediate (about 400 ps) lifetime were found to be only little sensitive to $O_2$ content. For PET applications, more detailed studies of positron annihilation in differently oxygenated tissues would be needed. In order to understand physical processes leading to little sensitivity of o-Ps lifetime on the chemical structure of liquids, a theoretical derivation of positron lifetimes from cross sections for isolated molecules is needed.

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